

Acetylation of Cotton Stalk for Cellulose Acetate Production

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Abstract

Cellulose acetate polymers were developed from pretreated cotton stalk (cellulose). The cellulose was acetylated through reaction with acetic acid and acetic anhydride in the presence of sulphuric acid as catalyst. The relationship between reaction time, catalyst loading and temperature on the weight percent gain and percent acetyl content of the cellulose acetate were investigated. Optimization of process conditions for acetylation via response surface methodology (RSM) revealed that the maximum weight percent gain (WPG) and percent acetyl content (PAC) were 50.79% and 43.73% respectively. The corresponding optimum operating conditions were 2.76 hrs, 6.09 wt% and 40.07 °C, for reaction time, catalyst loading and temperature respectively, while glacial acetic acid to cellulose ratio and acetic anhydride to cellulose ratio were 6:1 and 4.36:1 respectively. The result revealed that acetylation of cellulose extracted from cotton stalk was successful as indicated by the characteristic peaks in the Fourier Transform Infrared (FTIR) spectra and the decrease in the degree of crystallinity observed in the XRD patterns.

Keywords: Cotton Stalk; Acetylation; Cellulose Acetate; Response Surface Methodology; Optimization.

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1. Introduction

Increasing concern exists today about the preservation of the ecological systems. However, most of today's synthetic polymers are produced from petrochemicals and rarely biodegradable. Persistent use of polymers constitutes a significant source of environmental pollution, harming wildlife when they are dispersed in nature [1]. For example, the disposal of non-degradable plastic bags adversely affects sea-life. It is widely accepted that the use of long-lasting polymers in products with a short life-span, such as engineering applications, packaging, catering, surgery, and hygiene, is not appropriate. Moreover, incineration of plastic waste presents environmental issues as well, since it yields toxic emissions (e.g., dioxin). The potential of biodegradable polymers has been recognized for a long time since they could be an interesting way to overcome the limitation of the petrochemical resources in the future. The fossil fuel and gas could be partially replaced by green agricultural resources, which would also enhance the reduction of CO₂ emissions [2].

In Nigeria, enormous volumes of agricultural wastes that contain cellulosic fibers are generated annually. Many of these agro-wastes are allowed to rot away unutilized. For example, tonnes of maize stem, cobs from *Zea mays*, plantain stem, cotton stalks, raffia from *Raphia hookeri* are allowed to rot away. These agricultural wastes can be gainfully utilized in the production of wood pulp, cellulose and its subsequent conversion to cellulose derivatives for manufacture of plastics (biodegradable), photographic films [3].

The author in [4] established the process for obtaining cellulose acetate from agricultural by-products like corn fiber, rice hulls and wheat straw. The author in [5] carried out synthesis of cellulose acetate from cotton seed hulls and burr. Further work by the author in [6] who studied sugarcane baggase pretreatment with sulphuric acid as a step of obtaining cellulose. Also, the authors in [3] worked on the production of cellulosic polymers from oil palm trees, bamboo pulp, maize cob, stems from *zea mays*, and saw dust from pear wood. However, in all these works, there is limited information on the use of cotton stalk in producing cellulose acetate. With cotton production standing at 325356000lb.bales, as given by United States Department for Agriculture 2012, in Nigeria and cotton stalk being a renewable agricultural waste and constituting about 58.5 wt% of cellulose [7], it can adequately serve in the production of cellulose acetate when the cellulose is extracted.

Cellulose acetate is one of the oldest manmade macromolecules used extensively in the textile and polymer industries. It has an inherent advantage in that the starting material, cellulose, is a renewable natural resource. The current applications of cellulose acetate include textiles, cigarette tow, lacquers, cellulose films, and packaging. Since it is nontoxic, cellulose acetate is widely used in food packaging [1].

2. Experimental

2.1. Materials and reagents

The cotton stalk was obtained from Institute of Agricultural Research Farm (IAR), ABU Zaria, 98.5% acetic anhydride, 99.5% glacial acetic acid, 98% H₂SO₄ all analytical grades manufactured by BDH Chemicals, Poole, England were purchased from Haddis Chemicals, Samaru Zaria. Design Expert Software version 6.7 was employed in the experimental design, while FTIR spectrometer at National Research Institute for Chemical

Technology (NARICT), and XRD Machine (Nigerian Geological Survey Agency, Kaduna) were used for functional group study and morphological characterization respectively.

2.2. *Delignification of cotton stalk*

Pretreatment of agricultural waste is essential in order to remove lignin and hemicellulose, reduce the crystallinity of cellulose, and increase the porosity of the lignocellulosic materials [6 and 15]. The alkaline pretreatment using sodium hydroxide was implored following the method described by [21]. This was achieved by dissolving 5 g of the cotton stalk sample in 2 w/v% NaOH, the solution was heated at 40 °C for 45 mins. The solution was thoroughly washed with water until neutral pH was obtained and the sample was oven dried at 60 °C until constant weight was obtained. The same procedure was followed for 4 w/v% NaOH, ammonium solution and water.

2.3. *Acetylation of Cellulose*

Conventionally, acetylation is carried out by the reaction of glacial acetic acid as solvent with acetic anhydride as the acetylating agent in the presence of sulphuric acid as catalyst [3 and 8]. The reaction conditions depends on a number of factors which include temperature, time of reaction and concentration of catalyst that keeps varying to determine the optimum conditions for the acetylation. An experimental design using central composite methods (CCM) from response surface methodology of design expert software was used to study the best operating conditions (the temperature, concentration of the catalyst used and time of reaction). The acetylation was carried out by dissolving 5 g of pretreated cotton stalk sample in 10 ml glacial acetic acid and heated at 47.5 °C for 1 hr and 5 ml acetic anhydride was added with 5.5 wt% sulphuric acid as catalyst, the mixture is further heated for 1.5 hrs at the same temperature. The effect of varying the ratio of glacial acetic acid, acetic anhydride to cotton stalk was also investigated using the response surface methods.

2.4. *Weight percent gain and percentage acetylation determination*

Weight gain represents the increase in the weight of the pretreated cotton stalk when it was dispersed in glacial acetic acid as compared to the weight of the initial pretreated cotton stalk. This is necessary in order to determine the efficiency of the acetylation of the cellulose extracted from cotton stalk. After the completion of acetylation process, the acetylated cotton stalk was thoroughly washed to remove odour and any possible soluble impurities that may have accompanied the reaction process and it was then dried in an oven at 60 °C to constant weight. The weight percent gain was calculated using Equation 1 [8].

$$\text{Weight Percent Gain (WPG)} = \frac{W_{\text{final}} - W_{\text{initial}}}{W_{\text{initial}}} \times 100\% \quad (1)$$

Where W_{final} is the weight of the oven dried acetylated cotton stalk and W_{initial} is the weight of the oven-dried pretreated cotton stalk before acetylation.

Percent acetylation is the percentage of the acetyl group that has replaced the hydroxyl group in the pretreated sample based on titrametric procedure. The percent acetyl content was calculated using Equation 2 [9].

$$\% \text{Acetylation} = \frac{(B, \text{cm}^3) - (S, \text{cm}^3) \times N \times 4.305}{W} \times 100\% \quad (2)$$

Where B is volume of blank titration; S is volume of sample titration; N is 0.5, the molar concentration of both the acid and base used for the titration; 4.305 is related to the molecular weight of the acetyl group, the unit conversion from litres to millilitres, and fraction to percentage; W is the sample weight in grams.

2.5. Characterization

2.5.1. Fourier transforms infrared spectroscopy (FTIR)

The chemical investigation of functional groups in the pretreated cotton stalk (cellulose) and acetylated cotton stalk sample (cellulose acetate) were carried out using Fourier Transmission Infrared Spectroscopy (Spectrum Perkin Elmer). The sample disc was prepared by mixing and compressing the sample and KBr at a 1:1 ratio. FTIR spectra were produced by scanning at a 4 cm^{-1} resolution for transmission wavelength range 300 to 4500 cm^{-1} .

2.5.2. Wide angle x-ray diffraction (XRD)

The structural changes of polymers can be evaluated using XRD curves. So the XRD patterns of the pretreated cotton stalk and acetylated cotton stalk were obtained at room temperature with a scan speed of $4^\circ/\text{min}$ for 2θ ranging from 3° to 80° at a voltage of 40kV and current of 40mA.

The crystallinity of acetylated and pretreated cotton stalk was recorded on an X-ray diffractometer, Philips PW3040/60 (Netherlands), with CuK α radiation (wavelength of 1.5405 \AA). The measurements were carried out in 2θ ranges between 5 and 80 with step size of 0.026 and time per step 99.45s. The degree of crystallinity, shape and position of the cellulose peaks in the cotton stalk fibers were observed.

3. Results and Discussion

3.1. Design of experiments on acetylation process using central composite design (CCD)

The effect and interaction of reaction time (Y_1), concentration of sulphuric acid as catalyst (Y_2) and temperature of reaction (Y_3) over two observed responses: weight percent gain (WPG) and percent acetyl content (PAC) was analyzed using response surface methodology (RSM). Table 1 shows the complete design matrix of the Central Composite Design (CCD) and results of WPG and PAC as obtained from the laboratory.

3.2. Analysis of variance

Based on the result presented in Table 2, the analysis of variance showed that the predicted model is significant because the model F-value of 6.81 implies the model is significant and also the Prob > F = 0.0394 is less than 0.05. So the model can be used to navigate the design space. The fitted model for weight percent gain and percent acetyl content suitable for acetylation of cellulose are shown in Equation 3 and 4 respectively.

Table 1: Experimental design matrix and response of WPG and PAC

Run	Time (Hrs)	Concentration of H ₂ SO ₄ (%)	Temperature (°C)	WPG (%)	PAC (%)
1	2.50	5.50	47.50	48.5	41.6
2	1.00	10.00	60.00	11.3	23.6
3	4.00	1.00	35.00	23.4	38.5
4	5.02	5.50	47.50	34.7	31.9
5	4.00	10.00	35.00	30.8	32.7
6	1.00	10.00	35.00	26.6	29.6
7	4.00	10.00	60.00	17.5	24.8
8	4.00	1.00	60.00	13.8	24.4
9	2.50	5.50	26.48	40.1	38.4
10	2.50	5.50	47.50	48.5	41.6
11	2.50	5.50	47.50	48.5	41.6
12	1.00	1.00	60.00	16.8	20.5
13	2.50	5.50	47.50	48.5	41.6
14	1.00	1.00	35.00	18.9	29.5
15	2.50	5.50	47.50	48.5	41.6
16	2.50	5.50	68.52	16.8	23.4
17	0.02	5.50	47.50	15.5	21.5
18	2.50	5.50	47.50	48.5	41.6
19	2.50	13.07	47.50	13.2	20.2
20	2.50	2.07	47.50	10.2	18.5

Table 2: Analysis of variance (ANOVA)

	WEIGHT PERCENT GAIN	PERCENT ACETYL CONTENT
Std. Dev.	1.09	2.70
R-Squared	0.9973	0.9831
Mean	28.91	28.96
Adj R-Squared	0.9949	0.9679
C.V.	3.77	9.33
Pred R-Squared	0.9797	0.8676
PRESS	90.53	572.65
Adeq Precision	53.583	20.436
Model F value	416.21	64.68
Prob>F	0.0001	0.0001

The predicted Determination coefficient (Pred R-Squared) of 0.9797 is in reasonable agreement with the

adjusted determination coefficient (Adj R-Squared) of 0.9949 for WPG and that of 0.8676 to 0.9679 for PAC shows that the model is significant. This implies the 97.97% of variability in the data fitted to the model for weight percent gain and 86.76% for percent acetyl content. Also, the Prob>F = 0.0001 is less than 0.005, which equally shows that the model is significant [19 and 20].

The empirical mathematical model equation of the weight percent gain is shown in Equation 3

$$\text{WPG} = -91.62908 + 21.52932 Y_1 + 9.11423 Y_2 + 4.06419 Y_3 - 3.71622 Y_1^2 - 0.65647 Y_2^2 - 0.044915 Y_3^2 + 0.17407 Y_1 Y_2 - 0.040000 Y_1 Y_3 - 0.038667 Y_2 Y_3 \quad (3)$$

The fitted model for percent acetyl content is shown in Equation 4

$$\text{PAC} = -15.98305 + 14.96030 Y_1 + 3.33640 Y_2 + 1.52055 Y_3 - 2.03485 Y_1^2 - 0.35442 Y_2^2 - 0.019798 Y_3^2 - 0.15926 Y_1 Y_2 - 0.046667 Y_1 Y_3 + 0.020444 Y_2 Y_3 \quad (4)$$

Where Y_1 is the time of acetylation, Y_2 is the concentration of the sulphuric acid catalyst and Y_3 is the temperature of reaction.

3.2.1. Weight percent gain

Figures 1a-c display the three dimensional view and contour plots of WPG over reaction time, catalyst loading and temperature of the acetylation of cotton stalk. These figures show that the swelling time and catalyst loading have the most significant effect on the swelling rate of cellulose when dispersed in acetic acid compared to the temperature of the reaction. As illustrated in the Figure 1a, the cellulose started gaining weight at the start of the reaction when sulphuric acid catalyst is loaded and reached maximum around 5.5 wt% after which it became constant, beyond this point, there was no appreciable increase in the weight of cotton stalk but rather the degradation of the cotton stalk. On the other hand, Figure 1b displays the increase in WPG when the reaction time was increased. Temperature had a slight effect on the swelling rate of cellulose as observed in Figure 1b and c, the decrease in WPG noticed was due to the degradation of carbohydrates cellulose under strong acid condition and high temperature, which is in agreement with [10] observation that increase in temperature causes decrease in the swelling rate of cellulose.

3.2.2. Percent acetyl content

Figures 2a-c displays the three dimensional surface response for percent acetyl content as a function of two factors for experimental range considered during the acetylation of cellulose. As in the case of weight percent gain, concentration and time has the major significant effect in the substitution of hydroxyl group with acetyl group during acetylation. This was expected because the catalyst aids the reaction faster and the temperature effect helps in the mobility of the crystallites which are gradually broken down over a period of time. At catalyst concentration of 5.5 wt%, the reaction time of 2.50 hrs and reaction temperature of 47.5 °C the highest percent acetyl content of 43.73% was obtained. This percent acetyl content is higher than 40.3% and 39.0% as reported by the authors in [16 and 17] respectively when formulation effects on the thermo-mechanical properties of free

films and coating films and acetylation of mechanical pulp with subsequent isolation of cellulose acetate by differential solubility from wood pulp were studied. This indicated that the acetylated cellulose sample obtained at these conditions after washing had molecules with higher degree of acetylation as evident in the increased percent acetyl content.

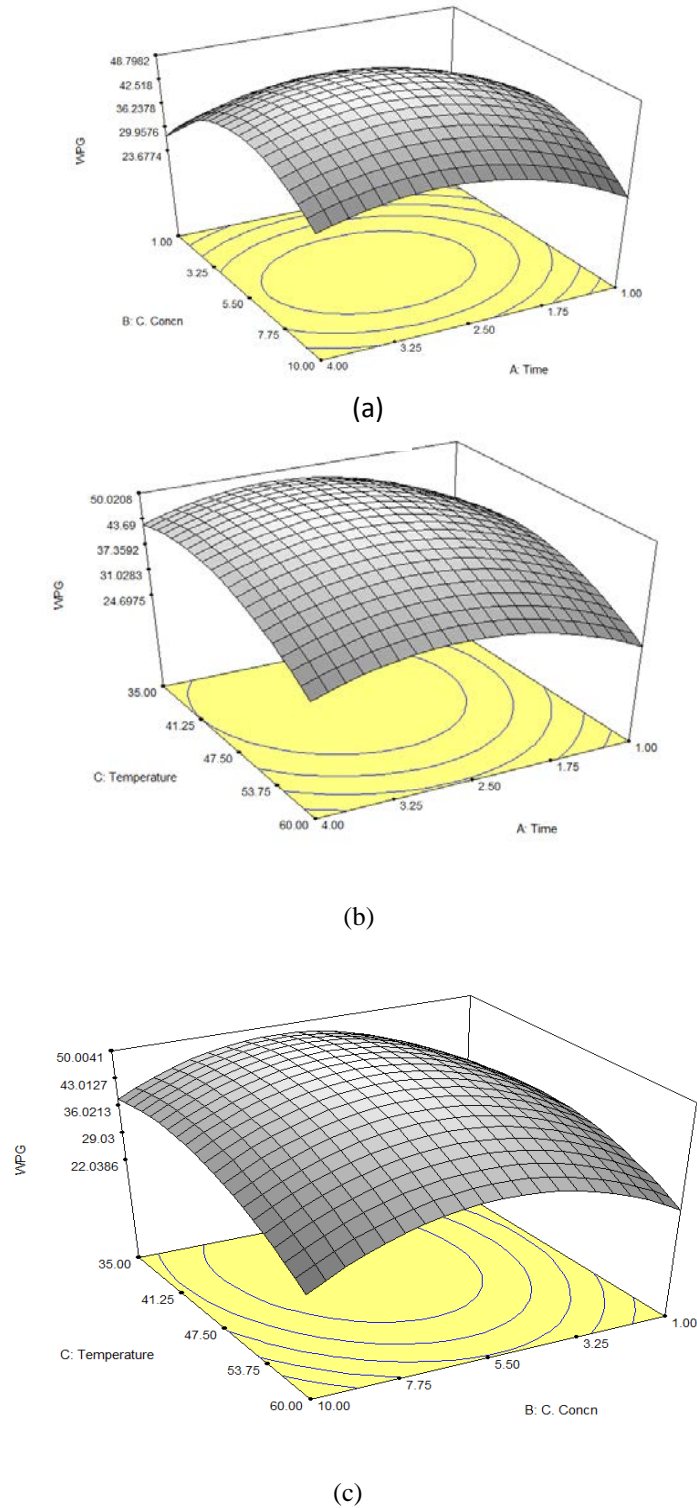


Figure 1: Response Surface Plot of WPG as a function of (a) Catalyst Loading and reaction time at temperature of 47.5°C (b) Temperature and reaction time at catalyst loading of 5.5wt% and (c) Temperature and catalyst

loading at reaction time of 2.5hrs.

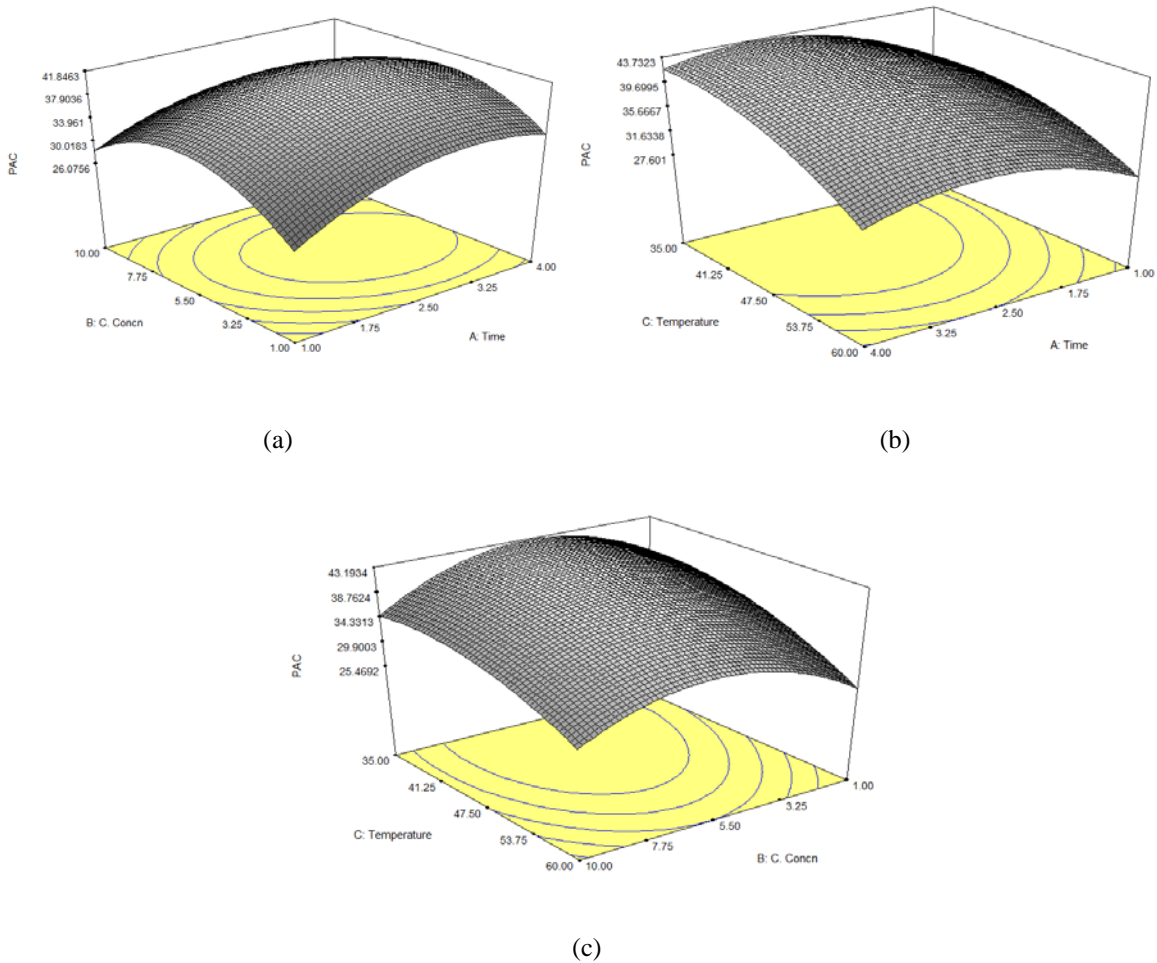


Figure 2: Response Surface Plot of PAC as a function of (a) Catalyst Loading and reaction time at temperature of 47.5⁰C (b) Temperature and reaction time at catalyst loading of 5.5wt% and (c) Temperature and catalyst loading at reaction time of 2.5hrs.

3.2.3. Effect of glacial acetic acid and acetic anhydride

The rate and perfection of acetylation is influenced greatly by the micro and macro morphology of the pretreated cotton stalk and the need for an effective acetylation of cotton stalk depends largely on the accessibility of the cellulose contents of the pretreated cotton stalk and also on the individual cellulose crystallites towards acetylation. Hence, the optimum process conditions obtained from the determination of weight percent gain and percent acetyl content were used to study the effect of varying glacial acetic acid and acetic anhydride ratio to pretreated cotton stalk sample. Figures 3a and b show the surface response of the weight percent gain and percent acetyl content.

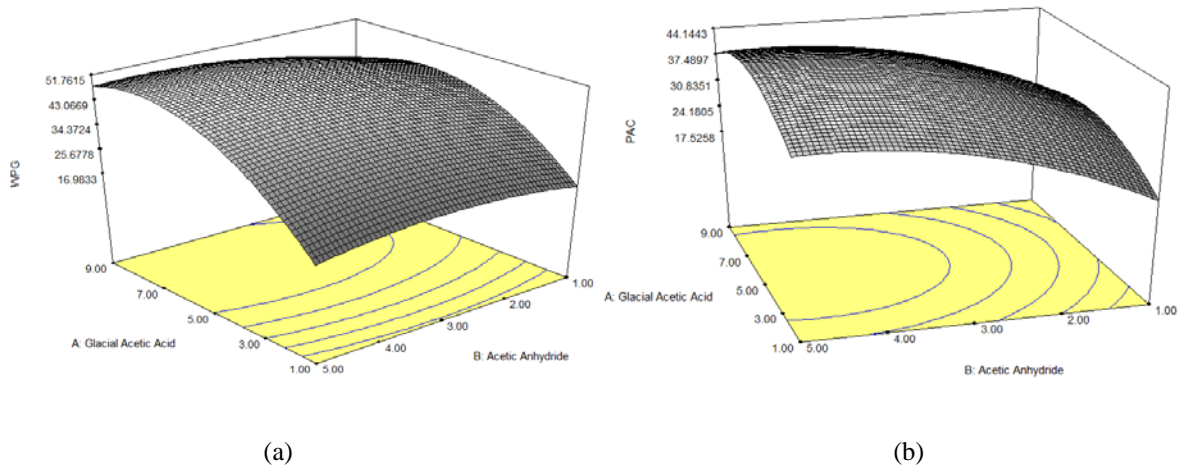


Figure 3 (a and b): Effect of Varying Glacial Acetic Acid and Acetic Anhydride to Cotton Stalk Ratio on WPG and PAC.

Figure 3a and b shows the effect of varying both glacial acetic acid and acetic anhydride to pretreated cotton stalk and it is clear that the weight ratio and percent acetyl content increased with increasing ratio of both glacial acetic acid and acetic anhydride. Glacial acetic acid is the solvent which functions as the swelling agent for the cotton stalk by increasing the accessibility of the cotton stalk hydroxyl groups to the acetylating agent (acetic anhydride). As evident from the plot, increasing solvent glacial acetic acid has significant effect on acetylation by increasing weight percent gain to 49.91% and percent acetyl content of 43.03% at 6.06:1 of glacial acetic acid to cotton stalk ratio at a corresponding ratio of 4.36:1 of acetic anhydride, but beyond that increasing the concentration of glacial acetic acid or acetic anhydride can cause degradation of carbohydrates which results in decrease in weight percent gain and mild increase in the percent acetyl content.

3.2.4. Optimization and validation of the model results

The model result obtained in this work was optimized and the response surface analysis using design expert software indicated that the predicted optimum WPG and PAC of cotton stalk acetylation is 50.79% and 43.89% respectively at 6:1 of glacial acetic acid to cotton stalk ratio and 4.4:1 of acetic anhydride to cotton stalk ratio at operating reaction time of 2.76hrs, 6.39wt% catalyst loading and temperature of 40.37⁰C.

Additional experiment was carried out to validate the optimization result obtained from the response surface analysis. The difference between the experimental results and the predicted values were slightly above the 5% level of significance which could be associated to some unavoidable experimental errors during the bench work.

3.3. Characterization of cellulose acetate (acetylated cellulose)

3.3.1. FT-IR spectroscopic analysis

Functional group changes after chemical modification of the pretreated cotton stalk was investigated by FTIR spectroscopy. The assignment of IR bands for different functional groups as given by [18] are in agreement with

the peaks obtained for this work.

Table 2: Validation of predicted model data

Factor					Response				
Time (hrs)	Conc (%)	Temp. (°C)	G. Acetic Acid (Ratio)	Acetic Anhydride (Ratio)	WPG		PAC		
					Predicted	Experimental	Predicted	Experimental	
2.76	6.39	40.37	6.06	4.38	50.79	47.09	43.89	41.76	
% Error					7.85%		5.100%		

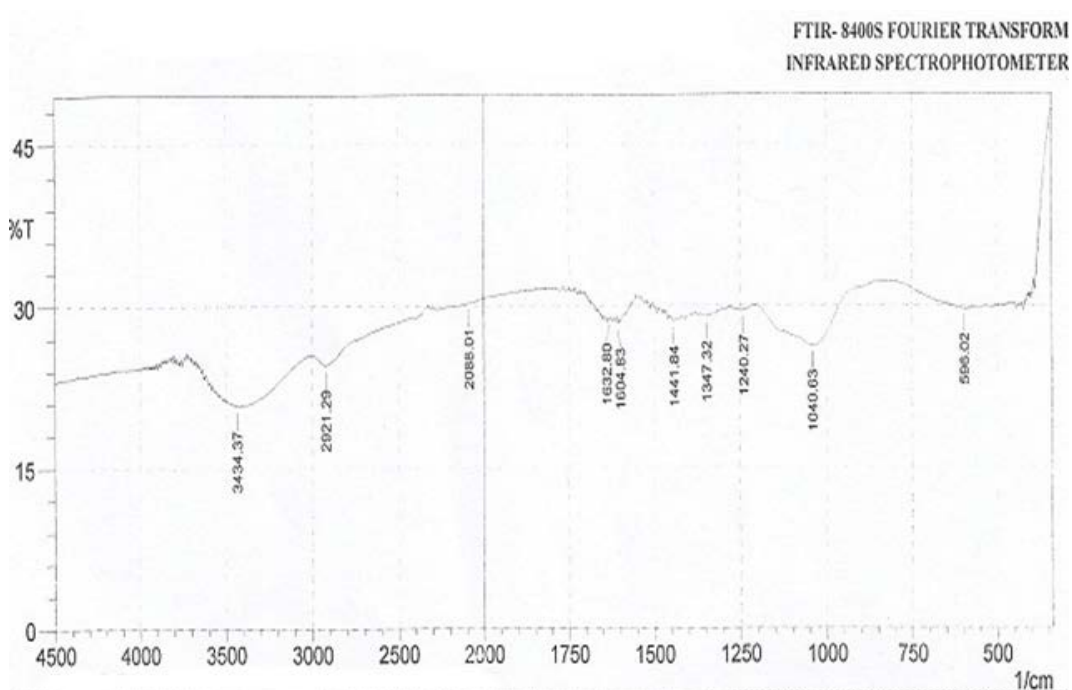


Figure 4(a): FT-IR Analysis of Pretreated Cotton Stalk

Figures 4a and b represent the FT-IR spectroscopy of the pretreated cotton stalk and acetylated cotton stalk. In Figure 4a, the absorption band at 3434.37 cm^{-1} is attributed to stretching vibrations of hydroxyl (-OH) groups present in the cellulose. The -OH groups may include absorbed water, aliphatic primary and secondary alcohols found in cellulose and hemicellulose extractives. When compared to Figure 4b, there is a decrease in the intensity of the -OH absorption band that the hydroxyl group contents in cotton stalk were reduced after reaction. The shoulder near the -OH stretching vibrations, 2921 cm^{-1} was attributed to C-H stretching vibrations and corresponds to the aliphatic groups in polysaccharides (cellulose). The ester carbonyl absorption peaks at 1746.60 cm^{-1} , carbonyl hydrogen (C-H) peak at 1374.36 cm^{-1} in acetyl group and 1230 cm^{-1} absorption (C-O) in O=C=O group verified ester bond have been formed in the acetylated cotton stalk and their relative intensity is enhanced. The characteristic peaks developed confirmed the acetylation of cellulose extracted from cotton stalk.

As observed in Figure 4b, there is no development of peaks or stretching in $1840 - 1760 \text{ cm}^{-1}$, this indicates the absence of free acetic anhydride in the acetylated cotton stalk under test. This is in agreement with the author's work in [11] where absence of free acetic anhydride was observed from the FT-IR spectra of modified rice straw for thermoplastic application.

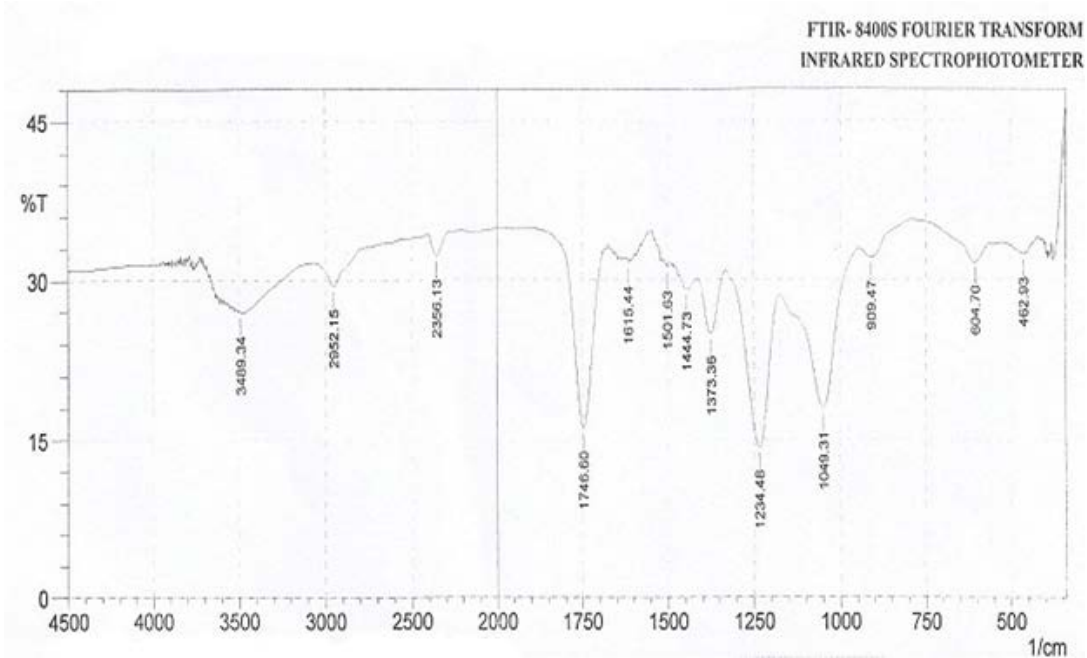


Figure 4(b): FT-IR Analysis of Acetylated Cotton Stalk.

3.3.2. X-Ray diffraction patterns

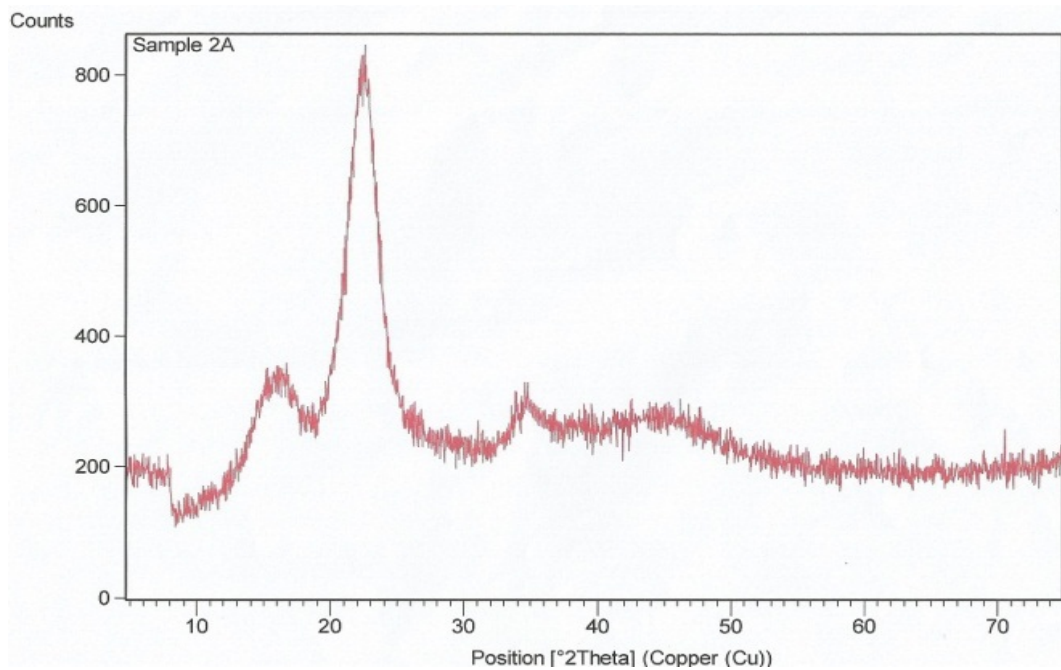


Figure 5(a): XRD Pattern of Pretreated Cotton Stalk

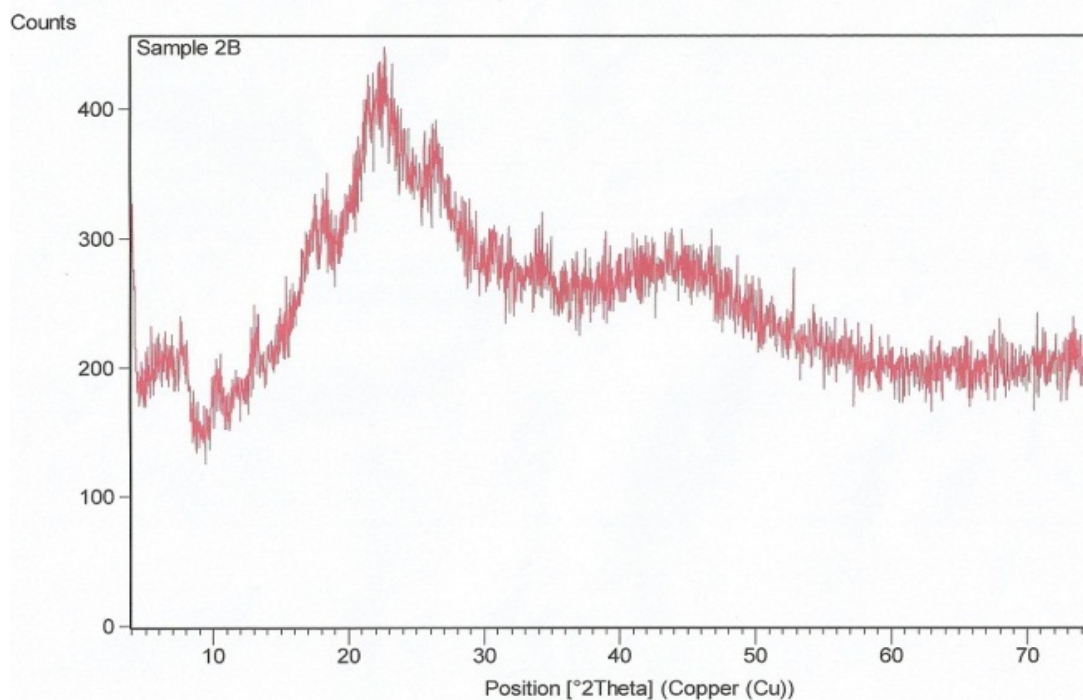


Figure 5(b): XRD Pattern of Acetylated Cotton Stalk.

The crystallinity of acetylated and pretreated cotton stalk was recorded on an X-ray diffractometer, Philips PW 3040/60 (Netherlands), with CuK α radiation (wavelength of 1.5405 Å). The measurements were carried out in 2 θ ranges between 5 and 50 with step size of 0.026 and time per step 99.45 s.

The x-ray diffraction patterns of the cotton stalk sample before and after acetylation are given in Figures 5a and b. As observed in the figures, the diffraction patterns of the cotton stalk changed after the chemical modification as evident in the reduction of the sharp peak at position 23[$^{\circ}$ 2Theta] in 5b when compared with 5a. The developed peak corresponds to that of Diana *et al.* [14] who presented the XRD patterns of cotton cellulose. As noticed from the plot, the acetylated cotton stalk (Figure 5b) has a low degree of crystallinity compared to that of cellulose (pretreated cotton stalk). The decrease in crystallinity is expected due to the degradation of the crystal structure of cellulose during acetylation [12], this is because the number of hydrogen bonds is decreased due to the substitution of hydroxyl groups by acetyl groups that have a larger volume and this confirmed why the acetylated sample is amorphous. As the cellulose chains at the surface are acetylated, they become soluble and removed, further exposing the cellulose crystals, which therefore reduces the crystallinity of remaining cellulose chains within the cellulose films as the acetylation continues [13].

4. Conclusion

The acetylation of pretreated cotton stalk is a typical heterogeneous process by the reaction of acetic anhydride in the presence of sulphuric acid as catalyst and glacial acetic acid as solvent. All the parameters such as reaction temperature, catalyst loading, reaction time, glacial acetic acid to cotton stalk ratio and acetic anhydride gave a significant effect on the acetylation process. Cellulose acetate was evidently produced as depicted by the

FT-IR and XRD analysis. The maximum cellulose acetate yield was obtained at glacial acetic acid: acetic anhydride: cotton stalk ratio of 6.06:4.36:1 respectively, with catalyst concentration of 6.39% at a reaction time of 2hrs:7mins:6sec and temperature of reaction of 40.37 °C. This gave a corresponding experimental weight percent gain of 50.79% and percent acetyl content of 43.73%, which is equivalent to 7.85% and 5.100% deviation from the model predicted values. This shows that acetylation of cotton stalk can be a simple procedure to develop an inexpensive and biodegradable cellulose acetate which can effectively replace raw materials from fossil fuels as starting material in polymer industries. The cellulose acetate produced can be casted into film used for packaging.

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